

Preparation of Cationic Functional Polymer Latexes and Measurement of Involatile Monomer Conversion

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ABSTRACT: A series of poly(styrene-*co*-methacryloxyethylhexadecyldimethyl ammonium bromide), P(St-DMHB), cationic particles were prepared by emulsion polymerization using 2,2'-azobis(2-methylpropionamide) dihydrochloride as the initiator with different levels of DMHB as the cationic functional comonomer. ζ potential, particle size, and size distribution of the particles were determined. Large discrepancy was observed between the particle size from dynamic light scattering and that from transmission

electron microscopy. Results showed that particle size and ζ potentials were closely dependant on DMHB level used. A flocculation process for the cationic latex was established, and a method to estimate DMHB conversion was proposed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3662–3668, 2012

Key words: emulsion polymerization; particle nucleation; particle size distribution; cationic latex stability; involatile monomer conversion

INTRODUCTION

Polymer latexes are widely applied in a great variety of industries, such as paints and coatings industries, textile and leather treatments, and paper industry. Interests in these areas have shown constant increase for nearly a century. It is to note that, among the myriad research reports published up to date, most of them have been focused on systems with anionic surfactants, which lead to anionic latex particles, namely, the surface of the particles is negatively charged. Studies on cationic latexes are obviously far behind their industrial development, and relative reports are far fewer compared to those on anionic latexes, although latex particles with their surface positively charged are also required in many cases such as oil-field drilling,¹ paper industries,^{2–4} and other areas.^{5,6} This situation has been changing. Interests in cationic polymer latexes have been in constant increase for the last decade, both fundamental and applied research are being reported.^{2–12} In a study on self-assembly of cationic and anionic latex particles through heterocoagulation,¹³ preparation of cationic latexes was attempted with different cationic functional monomers including dodecyl

benzyl dimethyl ammonium chloride, cetyl trimethyl ammonium bromide (CTAB) and methacryloxyethylhexadecyldimethyl ammonium bromide (DMHB), results revealed that only the latter two cationic monomers, that is, CTAB and DMHB, led to stable latexes with easily adjustable particle size. The preparation and properties of the cationic latex using CTAB have been reported.¹² Here, we report results on the cationic latexes prepared using DMHB. The effects of DMHB on latex properties including the particle size and its distribution, ζ potential, the stability of cationic latexes were investigated. More importantly, a method to determine the conversion of the involatile monomer DMHB was proposed based on a series of experiments.

EXPERIMENTAL

Materials

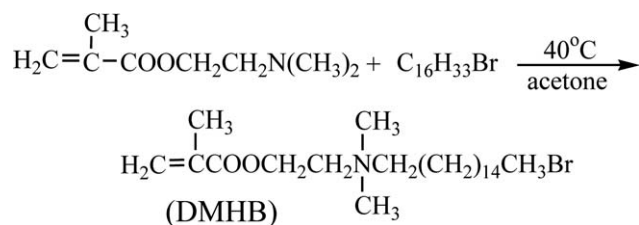
Styrene (St) was obtained from Tianjin Damao Chemicals and purified by distillation under reduced pressure in a nitrogen atmosphere before use. 2,2'-Azobis(2-methylpropionamide) dihydrochloride (AIBA, analytical grade) was from Du Pont of Japan. Ethanol (EtOH), acetone, butanone (MEK), hydroquinone, ethyl acetate, sodium chloride, and hydrochloric acid (HCl, 1.0 mol/L) were all analytical grade and used as received. Water was double-distilled and deionized. Dimethylaminoethyl methacrylate and *n*-hexadecanebromide, both analytical grades, were from Sinopharm Chemical Reagent.

Cationic functional monomer methacryloxy ethylhexadecyl dimethylammonium bromide (DMHB)

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Scheme 1 Preparation of methacryloxyethylhexadecyl dimethylammonium bromide (DMHB).

was synthesized through the reaction between dimethylaminoethyl methacrylate and *n*-hexadecanebromide as schematized in Scheme 1. The full details for the preparation and the characterization of the target product have been previously described.^{13,14}

Preparation of cationic P(St-DMHB) latexes and particle size determination

The P(St-DMHB) cationic latexes were prepared as described below. About 1.5 g of DMHB, 240.0 g of water, and 28.5 g of monomer St were added into a four-necked round-bottomed flask reactor of 500 mL equipped with an agitator, a nitrogen inlet, and a condenser with an outlet to a bubble counter. The content of the reactor was stirred for about 20 min at 800 r/min in order to get a completely homogenized emulsion, followed by locating the reactor into a water bath with temperature set at 70°C. The reactor was kept stirred for another 15 min at 250 r/min, and 30 mL of aqueous solution of the initiator AIBA (0.25 wt % concentration) was added to initiate the polymerization, which lasted usually 4 h. Nitrogen was bubbled into the reactor during the whole process. Latexes with different amounts of cationic monomer DMHB were prepared using the same setup and procedure with total amount of St and DMHB kept unchanged.

To determine the particle size, latex sample was diluted to a solid content of about 0.05%. Particle size, size distribution, and ζ potential were determined using dynamic light scattering (Malvern, nano-ZS). It is known that the particle size given by Malvern instrument is a *Z*-average (D_z , also known as the cumulants). The measurement is done by backscatter detection, which collects the scattering information at 173°. Through the cumulants analysis, the instrument gives also a width parameter known as polydispersity index (PDI), which is a number indicative for particle size distribution. For monodisperse latex, PDI is null; and for very broad size distribution, the maximum of PDI is one as defined by the instrument.

It is well known that particle size obtained from light scattering represents the hydrated size of the particles, which is often much larger than the *de facto*

size of the particles. Therefore, the latex particle size was also determined using transmission electron microscopy (TEM). The diameters of more than 200 particles on TEM micrographs were measured, and the number average size (D_n) and weight average size (D_w) were calculated using the equations below:

$$D_n = \frac{\sum_{i=1}^k n_i D_i}{\sum_{i=1}^k n_i} \quad D_w = \frac{\sum_{i=1}^k n_i D_i^4}{\sum_{i=1}^k n_i D_i^3}$$

D_w/D_n is the size distribution as commonly known.

Determination of latexes solid content and monomer conversion

Latexes solids were determined gravimetrically. However, it is commonly known that only the conversion of St, the volatile monomer, can be obtained from the solid content by deducting the contribution of DMHB to the solids, because DMHB is not volatile, and will remain in the sample when latex solid is gravimetrically determined. With objective to have an estimate on DMHB conversion in the polymerization, a protocol was designed, which constituted three steps: (1) Getting the latex completely flocculated; (2) repeatedly washing and filtering the flocculate with abundance of water in order to get rid of the soluble components, including residual DMHB and its homopolymers; (3) getting the final flocculate fully dried in an oven at 100°C till constant weight. Because only the soluble components in the flocculate could be washed away, the final flocculate was considered to be either St homopolymer or its copolymer with DMHB. A total conversion of St and DMHB was thus obtained. The conversion of DMHB was obtained based on these results and in combination of the St conversion obtained from gravimetry or gas chromatograph.

Denoting the weight of a latex sample as m_1 , the weight of the dried flocculate obtained as described above as m_2 , the latex solids contributed by the flocculate (with soluble DMHB monomer and oligomers deducted) as S , conversion of DMHB (C_{DH}) was calculated through the following equations:

$$S = \frac{m_2}{m_1} \times 100\%$$

$$C_{\text{DH}} = \frac{S \times m_0 - C_{\text{st}} \times m_{\text{st}}}{m_{\text{DH}}} \times 100\%$$

where C_{st} represents the conversion of St, m_0 the weight of total latex, m_{st} the weight of St charged in the polymerization system, and m_{DH} that of DMHB.

The validity of the process was checked. To a latex sample of known accurate weight, different amount of DMHB was added, the sample was kept stirring for 12 h at room temperature to make sure of complete dissolution of the added DMHB, and followed by the same process of latex flocculation and

TABLE I
Cationic Latexes Prepared at 70°C with Different DMHB Amount

Latexes	DMHB ^a (wt %)	D_z^b (nm)	PDF ^c	ζ potential (mV)	D_n^d (nm)	D_w/D_n
C1	0.25	105.7	0.037	37.7	74.3	1.044
C2	0.5	101.2	0.068	38.7	63.3	1.045
C3	1.0	85.1	0.089	45.4	52.9	1.034
C4	2.0	76.1	0.024	46.6	42.4	1.086
C5	3.0	67.3	0.033	46.3	39.1	1.055
C6	5.0	61.0	0.034	45.9	33.3	1.125
C7	10.0	51.6	0.079	46.9	29.5	1.075
C8	15.0	43.3	0.054	45.9	28.8	1.147
C9	20.0	42.5	0.086	46.2	28.1	1.153

^a Amount of DMHB (wt %) based on the total mass of monomers, St and DHMB.

^b Latex particles determined by dynamic light scattering with 0.01M NaCl solution.

^c Particle size distribution.

^d Latex particles determined from TEM micrographs.

washing. The finally dried flocculate was compared to that obtained without DMHB addition to see if the process was effective to get rid of the residual DMHB. St conversion by gas chromatograph was done on a Shimadzu instrument (GC-14C) with a 30 QC3/AC1 column (30M × 0.32 mm × 0.25 μm).¹⁵

Flocculation of the latexes

To obtain DMHB conversion, a reliable process for latex flocculation must be established as described earlier. Flocculation of P(St-DMHB) latex was first attempted by freezing the sample at -18°C overnight (>12 h) and allowed it to thawing at room temperature. The expected full flocculation did not occur. The flocculation was then tested with addition of a flocculant, HCl, or its mixture with another solvent. Complete flocculation was achieved when either a binary mixture of HCl/butanone (MEK), or a ternary mixture of HCl/MEK/EtOH was used at equal volume fraction.

RESULTS AND DISCUSSION

Effect of DMHB dosage on P(St-DMHB) cationic latexes

A series of P(St-DMHB) cationic latexes were prepared using the protocol described in the Experi-

mental section at varied DMHB levels while the other ingredients kept constant. Some properties of the latexes and of the latex particles were determined and listed in Table I.

From Table I, it is well seen that the particle sizes in the final latex regularly decreased from 105.7 to 42.5 nm when the amount of the functional monomer DMHB increased from 0.25 to 20.0 wt % based on the total monomer amount. This decrease in particle size with increasing DMHB was expected. As the functional monomer, DMHB was playing a dual function in the polymerization: a comonomer to copolymerize with St and a surfactant to stabilize the latex particles. The presence of a larger amount of DMHB would create a larger number of micelles before polymerization, leading to a larger number of particle nucleations, on one hand; and on the other hand, it would also endow the particles with more cationic groups on their surface, leading to a higher stability for the particles. In both cases, this would result in a smaller particle size as seen in Table I. It is easy to conceive that the surface charge on the latex particles thus prepared would be deficient when very low DMHB was used, characterized by a low ζ potential on the latex particles as observed for latexes C1 and C2. However, ζ potential of the particles quickly became constant after a peak value in sample C4 (2.0 wt % of DMHB) regardless of the continuous increase in DMHB level, indicating

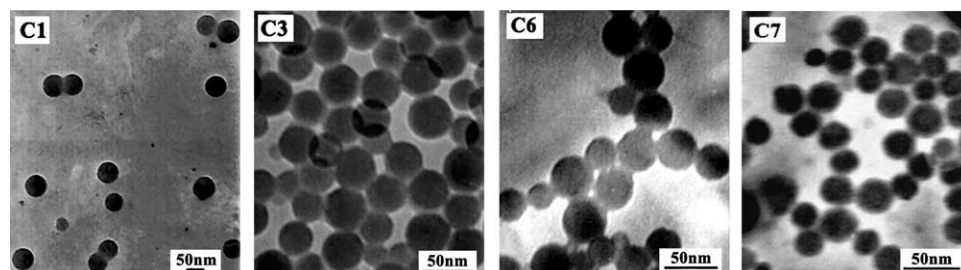


Figure 1 TEM photographs of cationic latex particles prepared with different DMHB levels (DMHB content: C1, 0.25 wt %; C3, 1.0 wt %; C6, 5.0 wt %, and C7, 10.0 wt %).

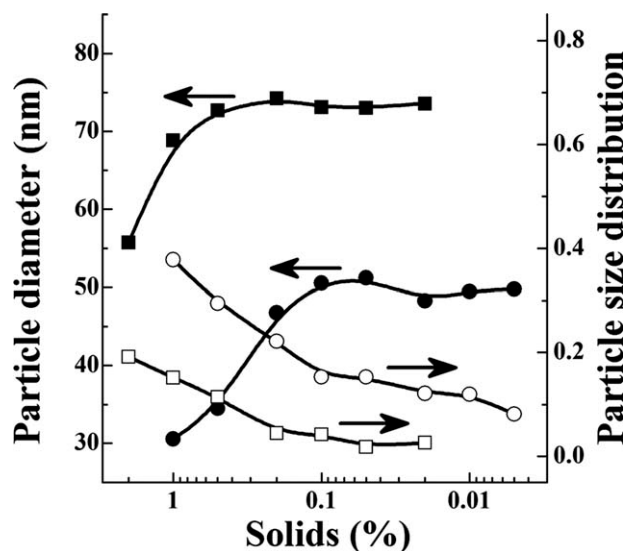


Figure 2 Evolutions of particle diameter (solid symbols) and size distribution (void symbols) with dilution of the cationic latexes prepared with DMHB levels of 2.0 wt % (C4, squares) and 10.0 wt % (C7, circles).

probably that the surface charge on the particles was no more deficient at this point. And more DMHB added afterward was used to create more particles, because the size of the particles was in constant decrease beyond this point. There are given two series of particle size in Table I, D_z and D_n , the former determined by light scattering, and the later from TEM micrographs. It is worth to note that D_z was significantly larger than D_n . This has been observed quite often^{16,17} and attributed to the fact that D_z represents the hydrated size of the particles. The presence of more hydrophilic groups with a higher density on particle surface will always give a larger particle size D_z than D_n , the *de facto* size of the dried up particles.

For a visual clarity, in Figure 1 are shown some TEM micrographs of the latex particles prepared using different DMHB amounts, which confirms the dependence of the particle size on DMHB level shown in Table I. Figure 1 also reveals that the particle size distribution, D_w/D_n was enlarged with

increase in DMHB, also in good agreement with the results in Table I.

Effect of latex solids on particle size determined by light scattering

In one of our previous study on cationic latex using CTAB as the cationic surfactant,¹² it was found that some latex properties, ζ potential, latex surface tension, and particle size determined by light scattering for instance were very sensitive to the actual amount of cationic surfactant on the particle surface, which was in turn closely related to the latex solids. By consequence, these properties were dependent on latex solids. When it comes to the present case where a functional monomer DMHB was used instead of CTAB, a no-polymerizable surfactant, the dependence of these properties on latex solids was also studied. It was found that ζ potential and particle size were in fact significantly affected by the latex solids, particularly for the latexes with high DMHB, although the cationic ammonium end groups were assumingly attached onto the particle surface by chemical bonding rather than by adsorption as was the case for CTAB. Figure 2 displays the variation of particle size versus latex solids along with the corresponding size distribution as an example.

Figure 2 shows clearly that the particle size of the latex C4 (prepared with 2.0 wt % DMHB as shown in Table I) was significantly larger than that of the latex C7 (prepared with 10.0 wt % of DMHB). As to the particle size evolution with latex dilution, both latexes exhibited similar profile: at high latex solids (1.0% or higher), the particles were characterized by small size. This size sharply increased when the latex was diluted to solids around 0.1%, reaching the final and highest values for particle size, which remained unchanged afterwards regardless of the further dilution. Concomitantly with the particle size evolution, the size distribution also became narrower with latex dilution. Based on the observations, the aggregate or combination of latex particles at high solids was excluded, because aggregation of latex particles should give larger particle size rather than

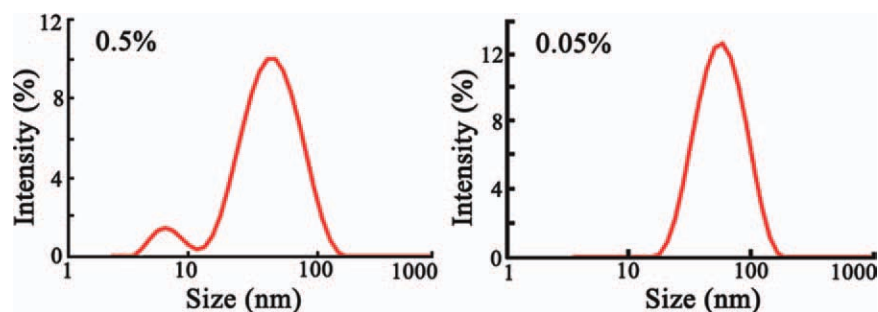


Figure 3 Particle diameter distribution in cationic latex with 15.0 wt % DMHB (C8) at solid content of 0.5% (left) and 0.05% (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

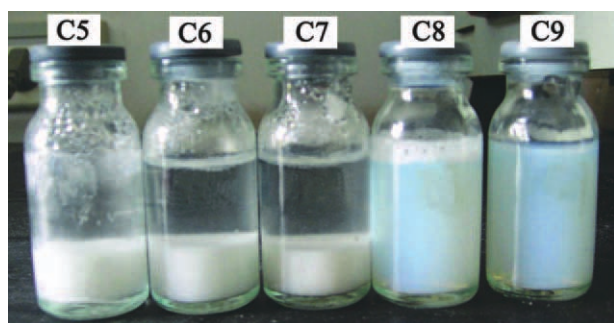


Figure 4 P(St-DMHB) latexes of different DMHB levels upon freezing at -18°C and thawing (DMHB content: C5, 3.0 wt %; C6, 5.0 wt %; C7, 10.0 wt %; C8, 15.0 wt %; C9, 20.0 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

smaller one, and this sort of aggregation would occur only when functional groups on particle surface were deficient, which, obviously, was not the case in the present system. The observation of the smaller particles at high solids was therefore believed to be attributable to the eventual presence of soluble components consisting of residual DMHB and its homopolymers. These water-soluble components must be abundant seeing the rich amount of DMHB used (see next section for the determination of DMHB conversion) and should form micelles or alike at high latex solids. With latex dilution, these aggregates of the soluble components will disassemble and dissipate into the surrounding water phase just like the case to dilute a surfactant solution from above its critical micelle concentration (CMC) to below its CMC. The size distribution of latex C8 was measured at different solids and displayed in Figure 3 for a visual illustration. This figure shows clearly that there were two distinct groups of particles detected at 0.5% solid content, one with an average diameter of about 8 nm, corresponding to the size of the micelles of ionic surfactants, and another with a peak distribution at about 50 nm. The group of the small-sized particles at 8 nm disappeared once the latex diluted to 0.05% solid, which was considered as an evidence that these small particles were composed of aggregates of DMHB or its oligomers, a good support to the above conjecture.

The results in Figures 2 and 3 lead us to conclude that, in order to get reliable result on particle size, the solid content in a latex sample should be kept

TABLE II
Effect of Flocculant on the Stability of Cationic Latexes with 15.0 wt % DMHB

Flocculants (equal volume in the mixture)	Flocculate appearance	Filtering observation	Filtrate
HCl (1 mol/L)	Polymer grits	Hard	Light blue
HCl/EtOH	Polymer grits	Hard	Light blue
HCl/acetone	Polymer grits	Easy and quick	Translucent
HCl/MEK	Coagulum	Easy and quick	Transparent
HCl/MEK/acetone	Polymer grits	Hard	Translucent
HCl/EtOH/MEK	Coagulum	Easy and quick	Transparent

below 0.1% or lower. All tests in this work were done this way.

Flocculation of P(St-DMHB) latex

In the latex stability test, the freezing-thaw was first carried out on P(St-DMHB) latexes of different DMHB level. It was found that the flocculation was not complete, only partially flocculation was achieved for latexes with low DMHB with phase separation after about 5 h shelf standing upon thawing, whereas no phase separation occurred for those with 15.0 wt % DMHB (C8) or higher, as visually illustrated in Figure 4. It is noted that it was difficult to process the phase containing the flocculated polymers at bottom of the bottles, because the polymer-containing phase was viscous and hard to be filtered or washed with water.

Experiments were then continued with chemical solvent to break down the latex. Reports on flocculants for cationic latex are rarely available, though those on anionic latexes are numerous. To start the tests, HCl of 1 mol/L concentration or its binary or ternary mixtures with a number of solvents were tested on the latex sample C8 (with 15.0 wt % DMHB) in Table I. In all tests, 60 mL of the flocculant was added to 7.00 ± 0.15 mL of latex sample with solid content around 10%. Results and observations are summarized in Table II.

It is seen from Table II that most of the tested flocculant was not effective, the yield flocculate was under form of small grits of polymers, and the filtrate was not fully transparent, which were indications that the

TABLE III
Conversion of DMHB in Different Emulsion Polymerization

Latexes	DMHB (wt %)	Latex solid (%)	St conversion (%)	Polymer flocculate (%)	DMHB conversion (%)
C6	5.0	9.53	95.1	9.42	78.0
C7	10.0	9.67	96.3	9.29	62.5
C8	15.0	9.57	94.9	8.97	60.0
C9	20.0	9.71	96.4	8.84	56.5

TABLE IV
Tests on Effectiveness of Latex Flocculation with Different Amounts of Flocculant (HCl/EtOH/MEK) and of Supplemented DMHB

Runs	D2	D3	D4	D5	D6	D7	D8	D9
Flocculant (mL)	60	60	60	60	30	60	90	120
Latex (m , g)	7.1931	7.0086	7.0128	7.0238	7.1024	7.1432	7.0207	7.0895
Added DMHB (g)	0.0108	0.0296	0.0504	0.0703	0	0	0	0
Involatile (m_i , g)	0.7013	0.7024	0.7236	0.7446	0.6818	0.6857	0.6740	0.6806
Flocculate (m_f , g)	0.6397	0.6318	0.6227	0.6286	0.6406	0.6400	0.6326	0.6381
m_f/m_i (%)	91.21	89.95	86.06	84.42	93.96	93.34	93.86	93.76
m_f/m (%)	8.89	9.01	8.88	8.95	9.02	8.96	9.01	9.00

cationic particles with excessive DMHB were quite stable. By consequence, the separation of the flocculate from the supernatant by filtration was hardly processible. However, effective flocculation was indeed observed when mixture of HCl and MEK at equal volume was used, which gave large blocks of flocculate, and fully transparent filtrate after a quite easy and rapid filtration. It was observed that HCl was not fully miscible with MEK, and phase separation appeared soon after stirring halted. Ethanol was then added to the binary mixture to make a ternary flocculant at equal volume, with which equal effectiveness to the binary flocculant based on HCl and MEK was confirmed in flocculating the cationic latex. This ternary solvent flocculant, HCl (1 mol/L)/EtOH/MEK (1/1/1 by volume), was used in all the tests.

Determination of DMHB conversion

Through the process described earlier, DMHB conversions in copolymerization with St using different DMHB amounts were determined. The results are listed in Table III, which shows that DMHB conversion was decreasing with increased DMHB in the polymerization. The highest conversion was of 78.0% when 5.0 wt % of DMHB was used. Knowing that the homopolymer of DMHB was very plausible to be washed away, actual conversion of DMHB might be slightly higher than those shown in Table III. These data indicate that DMHB is not as active as St is in the polymerization, at least this must be true with regard to its activity of copolymerization with St.

It is easily understood from above discussions that the reliability of the DMHB conversion depends on the effectiveness of the process to sweep off residual DMHB and, at the same time, to keep the most of the polymer possible in the flocculate. To further confirm this point, an accurate amount of DMHB was added into a given latex sample with known solids of 9.60% (a repeated run of C8, with 15.0 wt % of DMHB), and the latex was flocculated using varied amounts of flocculant, that is, HCl/EtOH/MEK mixture at equal volume. The final flocculate was weighed (m_f), and the ratios of this retained polymer flocculate versus the total involatile (m_f/m_i)

and that versus to original latex (m_f/m) were all given in Table IV.

The last four columns (samples D6–D9) are the tests on the amount of flocculant without DMHB addition, which revealed clearly that the polymer flocculate was indeed reproducible. Among the four samples, an average of 93.73% of the involatile components was remained as the polymer flocculate, which means that 6.37% of the involatile components were washed away through the process. The largest deviation from this average was 4.0%. Knowing that 15 wt % of DMHB relative to all monomers was used and that St was nearly 100% polymerized, this indicated that about 42% of DMHB was washed away, which gave a DMHB conversion of 58%, very close to that found in run C8 (Table III).

Another set of experiments (samples D2–D5 in Table IV) was also designed with the addition of different amounts of DMHB into the same latex prepared with 15.0 wt % of DMHB. All these samples therefore possessed the same polymers but different DMHB. The samples were treated through the same process. The flocculate (m_f) was collected and the ratios of the flocculate to the total mass of the latex (m_f/m) given in Table IV, which shows that this ratio was practically the same for all the four samples regardless of the added DMHB. This indicates that the added DMHB was all washed out, which provides a solid support to the effectiveness of the process, and the DMHB conversion thus obtained is highly reliable.

CONCLUSIONS

Cationic latexes based on P(St-DMHB) with different DMHB were prepared by emulsion polymerization. Results showed that particle size of the latex became smaller with more DMHB used, while the size distribution became broader at the same time. A significantly larger particle size was obtained from light scattering than from TEM, due to hydration of the cationic groups on particle surface. The cationic latexes were all of high stability and survived freezing-thawing test. A mixed solvent based on HCl/butanone/ethanol at equal volume was found to be

an effective flocculant for the latex. Based on the results, a protocol to estimate the conversion of the involatile DMHB was established and its reliability successful tested.

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